Synopsis of Proposed Ph.D. Research Work

Title of the Proposed Thesis:

Synthesis, Structural, Electrical and Magnetic Properties of Transition Metal Oxides

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Table of Contents

Origin of the Research Problem: 3
Objective of the work: 5
Methodologies: 6
Solid state synthesis 6
Solvothermal or hydrothermal technique 6
Sol-gel technique 7
Future Prospect 8
References: 8

Origin of the Research Problem:

Investigations on transition-metal oxides demand attention of materials community over half a century. The transition elements are those elements in the periodic table which are having incomplete *d* shells and among them the most important elements are Ti, V, Cr, Mn, Fe, Co, Ni, Cu with the atomic numbers ranging from 22-29. The compounds they make with oxygen present a variety of properties like superconductivity, colossal magnetoregistance, multiferroism as well as ferroelectricity in d^0- type oxides, d^0- type ferromagnetism, thermoelectric property and so on. Transition metal oxides are also technologically important materials and they have lot of applications.

The transition-metal oxide systems are shown to exhibit a wide range of intriguing physical properties.[1-3] Accordingly, it was realized that they could have a great potential as functional materials for real application purpose. However, the proper understanding of such remarkable physical properties exhibited by transition metal oxide systems is rather complicated. Unlike most other solids, their properties cannot be rationalized within the framework of usual one electron band theory. This is mainly due to the strong electronic correlation between the various degrees of freedom available in the condensed system. Such degrees of freedom are mainly spin, charges/valence, orbitals and lattice. The interest to the correlated system arises after the discovery of high-temperature superconductivity in the layered cuprates in 1986.[4] Another extraordinary achievement from the study of the first series of the transition elements is the discovery of colossal magnetoresistant (CMR) in manganese oxides with the perovskite structure, leading to possible applications in the field of magnetic energy storage and as sensors and activators. However, the discovery of these effect calls for a new physics to be explored, which requires a better knowledge of the complex solid state chemistry of these oxides. The strongly correlated systems form a major part of the research topics in the field of modern condensed matter physics, chemistry and materials science. In this context, recently multiferroic materials have attracted a significant attention of the materials community. Mutiferroic materials are the novel class of next generation multifunctional materials with the panorama of a variety of device applications. Their multifunctionality appears due to cross-coupling phenomena between magnetic spin, electric dipole and ferroelastic ordering coexisting simultaneously in a single-phase material.

Multifunctional materials (multiferroics, magneto dielectric, spintronics etc.) have attracted increasing attention due to their possible application toward storage materials and intriguing fundamental physics. Among the naturally existing oxides, the presence of both ferromagnetic (FM) and ferroelectricity (FE) is a rare phenomenon, due to the incompatibility between magnetism and ferroelectricity. This incongruity could be at the origin of a limited number of ferroelectromagnets, though the researchers are looking for such materials from more than six decades. This phenomenon often occurs in perovskite oxide having the general formula ABO_3. In the process of exploration of a multiferroic perovskite the following facts are now well established: (i) FM and FE are mutually exclusive due to the d^0 electronic structure of the B-site element,[5] (ii) the occupation of different B -site cations with varying ionic radius provide an opportunity to realize a polar ground state,[6] and (iii) the lattice distortion induced by cations with lone pair electrons such as Pb^{2+} or Bi^{3+} which play a primordial role on the FE properties as reported for $PbTiO_3$ in comparison with $BaTiO_3$.[7-8]

The most well-known examples of existing perovskite multiferroics are $BiFeO_3$[9] and $BiMnO_3$.[10] A larger number of investigations carried out on both these oxides revealed that $BiFeO_3$ is a canted antiferromagnet, which gives rise to weak ferromagnetism and the latter is metastable, requiring high pressure conditions for synthesis of bulk phases.[7-8] Bi-based manganite perovskites, which show simultaneously ferromagnetic (FM) and insulating properties.[5-6] Actually, the ferromagnetic-semiconductors/insulators are novel singular materials that could exhibit simultaneously electric and magnetic ordering.[11]

Recently the magnetic semiconductor double-perovskite La_2NiMnO_6 has received considerable attention due to its relatively high Curie temperature (Tc) ~280 K.[12] More importantly La_2NiMnO_6 exhibits a colossal magnetodielectric coupling (up to ~20%) for a wide temperature range covering room temperature.[13-14] A giant tunability of dielectric permittivity was also reported in bulk La_2NiMnO_6.[15] In contrast to the conventional ferroelectrics, such as $BaTiO_3$,[16] La_2NiMnO_6 exhibits low voltage tunability. The structure of La_2NiMnO_6 is rhombohedral at high temperatures and at low temperature it transforms to monoclinic or orthorhombic.[17-18] Both high temperature rhombohedral and low temperature monoclinic/orthorhombic phases coexist over a significantly wide temperature range, across room temperature.[19-21] The magnetic

structure of La_2NiMnO_6 is rather controversial. It is highly sensitive to the synthesis condition and relative ordering of the B-site cation.

It is worth investigation to find the functional materials of perovskite based simple or double perovskite transition metal oxides or other structural family oxides with possibility of showing appreciable coupling between magnetic and electrical order parameters. In this proposed work at the initial stage focus will be given to modify the simple or double perovskite structure like $La(Fe/Mn)O_3$ or La_2NiMnO_6 by chemical substitutions to tune the magnetic and/or electrical properties. Attention will be paid to achieve an appreciable magnetoelectric coupling at room temperature.

Objective of the work:

The synthesis, structural, electronic and magnetic properties of different perovskite and related oxides of transition metal will be investigated. The well-known perovskite multiferroics are $BiFeO_3$ and $BiMnO_3$ will be magnetically diluted with the titanium, zinc or magnesium like non-magnetic ions keeping in mind that the large ferroelectric behavior observed in $BaTiO_3$. It will be interesting also to look on orbital hybridization between the magnetic and non-magnetic B-site cations and its effect on structure-property.

The rock salt ordering of Ni^{2+} and Mn^{4+} octahedra in La_2NiMnO_6 follow a 180◦ ferromagnetic superexchange interaction. However, the properties are sensitive synthesis condition. Similarly the ordering of the two transition metal cations in the crystallographic lattice plays a crucial role in the magnetic and transport properties of the system.[12] The origin of magnetoelectric effect whether it is intrinsic or extrinsic in La_2NiMnO_6 is controversial. The intrinsic effect arises from spin-lattice coupling, magnetostriction, exchange striction, charge ordering etc whereas extrinsic effect are related to external perturbation like applied electric or magnetic field. To understand the high temperature ferromagnetic ordering, insulating characteristics and magnetodielectric effect of La_2NiMnO_6 we will chemically modify the compound to tune the physical properties and to avail the significant coupling at room temperature. We have substituted on both A- and B-sites and obtained structurally pure phase of orthorhombic symmetry. In A-site doping we replace La by Bi^{3+} which is expected to have s^2-lone pair and may affect the electron-lattice coupling. Several compounds with replacement of

tetravalent manganese by tetravalent titanium have been synthesized. The properties of these samples are will be measured and structure property relationship will be established. Such understanding will be helpful to design new materials of desired functionality.

Efforts will be given to synthesis the compounds in bulk as well as in nanodimension. A comparative study between the bulk and nanophase may underscore the microscopic origin of the observed physical properties and its relation to the structural feature.

Methodologies:

The material of desire composition will be selected based on chemical intuition and existing expertise. The compounds will be synthesized in a number of ways as given below. The structural and physical characterization will be carried out using powder x-ray diffractometer and physical properties measurements systems, respectively. Below are the details of various synthetic routes for the sample preparation.

Solid state synthesis

It is an age old technique to prepare solid solutions. In this technique the required stoichiometric precursor materials are intimately mixed using a mortar pestle and fired at successive increasing temperature with intermediate grinding to ensure the completion of the reaction. Finally the purity of the phase formed is checked with x-ray diffraction of the sample.

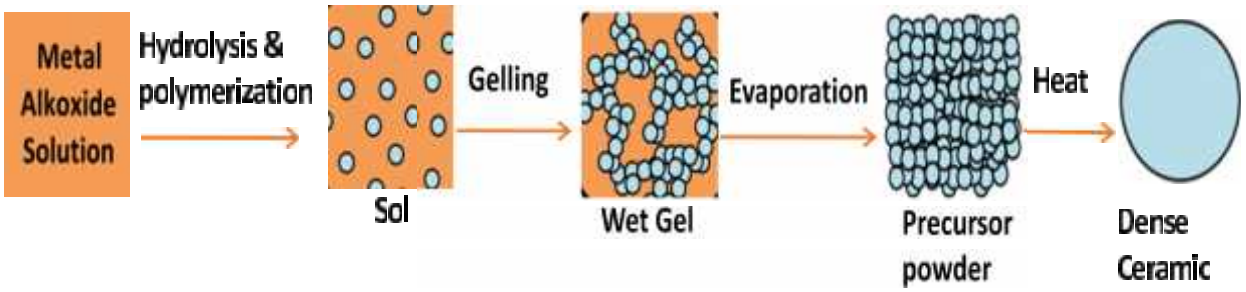
Solvothermal or hydrothermal technique

The solvothermal technique is being tremendously used for synthesizing oxide materials in recent years. The solvothermal or hydrothermal reaction can be considered as any heterogenous chemical reaction in the presence of a solvent (whether nonaqueous or aqueous) above room temperature and at pressure greater than 1 atm in a closed system. Hydrothermal processing is a very convenient technique for the preparation of various multicomponent oxide materials at moderate temperatures and pressures (>100°C and 0.1 M Pa) that have maximum utility in present day electronics applications.[20] The success of hydrothermal synthesis depends on the selection of precursors that are both reactive and cost effective as well as appropriate process condition variables, which include temperature, pH, and reagent concentration.[21] In the last

decade, hundreds of publications have appeared in literature devoted to various aspects for preparation of these perovskite type oxides owing to their potential applications in modern technology.[22-23]

Sol-gel technique

Metal alkoxides or even inorganic salts of the metal are popular precursor for the sol-gel synthesis.[24] The precursors undergo hydrolysis followed by condensation to form large molecules i.e. the polymerization (see scheme-1). If we prepare a solution of monomers and allow it to condense into crosslinked polymers with an average size of several nanometers, it will results a sol or colloids in which the dispersed phase consists of nonpolymeric solid particles. Sols needs to stabilize to prevent aggregation. On the other hand, gel is a substance that contains a continuous solid skeleton enclosing a continuous liquid phase. The continuity of the solid structure gives elasticity of the gel and gel can also be formed from particulate sols when attractive force dominates to stick then together in such a way to form a network. The gel is dried by evaporation to form powder and followed by annealing at required temperature dense ceramic is obtained. The whole process of sol-gel preparation of ceramic powder starting from metal alkoxides is shown in Scheme-1.



Scheme 1

Sol-gel technique offers the possibility to control the reaction pathways on a molecular level during the transformation of the precursor species to the final product, enabling the synthesis of ceramics powder, even nanodimensional ceramics with well-defined size, superior purity and uniform crystal morphologies. The sol-gel process precursor method provides several advantages

like controlling of the microstructure with relative ease, low processing temperature etc. There are several gelling agents like citric acid, polyvinyl alcohol etc. There are several reports on synthesis of pervskite oxides by sol-gel techniques.[25]

Future Prospect

Multiferroics combining different functionalities are currently a system of substantial research interest due to their long-term technological objectives which may lead to an expanding field of applications. The several simple and double perovskite oxides are promising multiferroic compounds. The direction of the future work will be taken based on the results and analysis of the results of the so far synthesized compounds. There are scopes to prepare composite materials of the different functionalities to execute the desire application. The proposed research work is targeted to find new compounds that will show room temperature magnetoelectric coupling. The establishment of structure-property relationship in these oxides will help to further develop new materials with capabilities to enhanced magnetic/electrical tunability.

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